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Municipal Environmental Research
Laboratory
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Research and Development

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Project Summary

Removal of Nitrate from Contaminated Water Supplies for Public Use: Final Report

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Gerald A. Guter

Three treatment processes (reverse osmosis (RO), ion exchange, and the combination of RO followed by ion exchange) to remove nitrate from public water supplies obtained from wells were evaluated. Laboratory size and field-test equipment was used to establish design criteria and operating experience useful for designing a full-scale plant of approximately 1-million gal per day (mgd) capacity. An interim report (EPA-600/2-81-029) on this project was published in February 1981 and is available from the National Technical Information Service, Springfield, Virginia; and the final report is summarized herein.

The program was conducted by the McFarland Mutual Water Co. at well No. 3 in McFarland, California. Ion exchange column tests were conducted with five strong-base anion exchange resins on nitrate-laden waters of various anion compositions. From this work, estimates of product water quality and the bed volume capacity for feedwater of any composition can be made. A working hypothesis was developed from an analysis of the data about how the chemical structure of resins can be practically altered to obtain nitrate selectivity. As a result, a series of resins was synthesized to study the effect of molecular structure on nitrate selectivity. Two of the resins showed selectivity of nitrate in preference to sulfate ion. Others in the series showed enhanced sulfate selectivity.

A 20-in. diameter pilot anion exchange column was designed and operated for over 1 year at well No. 3. Data from this column operation was used to verify estimates of pilot column performance and to project the cost for equipment and regenerant for a well site installation to treat up to 1 mgd. An RO system having a production capacity of 76 m^3/day (20,000 gpd) was operated for over 1,000 hours until excessive nitrate passage was obtained.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The small community of McFarland, California, in the heart of the intensive agricultural/industrial area of the San Joaquin Valley in central California, is faced with declining water quality and increased demand on their groundwater supply. This problem is typical of many communities not only in the United States but throughout the world. If the development of new water sources from surface supplies or deep aquifers or the use of centralized treatment is economically unfeasible, well site treatment for contaminant removal is an alternative to be considered. This study concerns

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applying treatment processes to a well site situation — and improving water quality without constructing new wells, modifying old wells, or altering the distribution system.

Well site treatment to remove nitrate is not considered to be standard practice; only a few such installations can be cited throughout the world, and no detailed operating data or costs have been published. Although ion exchange and reverse osmosis (RO) are familiar and widely used processes in industrial water treatment, their use to remove specific contaminants from community water supplies is new and requires the traditional demonstration project to advance widespread use of these processes. This study provides both engineering and scientific aspects information and data to aid the planning of a demonstration project. The engineerng aspects deal with design parameters, conceptual designs, operation, and process reliability derived from actual hands-on experience. The scientific aspects deal with ion exchange theory of resin selectivity and the testing of new resins that show nitrate selectivity in presence of sulfate and other common anions. It is believed this work has resulted in a major breakthrough in development of nitrate-selective resins having the potential to lower costs of nitrate removal for many communities. The method used to derive the nitrate-selective resins can be used to derive resins selective for other inorganic contaminants.

Methods and Materials

All tests were conducted at a well site (No. 3) owned and operated by the McFarland Mutual Water Company. Nitrate-nitrogen levels for this water were 16 to 23 mg/L, well above the 10-mg/L maximum contaminant level. Sulfate levels were greater than 300 mg/L.

Site improvements were designed for well No. 3 to accommodate equipment for conducting both field and laboratory scale experiments. Water was supplied directly to a concrete pad and trailer from an existing hydropneumatic tank. All product and wastewaters were discharged from the pad directly into the city sewer system. The 9.1- x 9.8-m (300- x 32-ft) pad was large enough to accommodate a field test ion exchange system, a field test RO system, and a single module RO system with the necessary tanks for temporary water storage. A trailer adjacent to the pad housed a field office and limited laboratory facilities.

A source of well No. 3 water was available in the trailer for experimental tests which were conducted on various ion exchange resins in 5.1-cm (2-in.) diameter columns. Synthetic mixtures were prepared and pumped directly at measured flow rates through the ion exchange columns. Five commercially available exchange resins were studied along with eight specially prepared resins. Because only the single-bed process was chosen for this study, tests were limited to strong-base anion exchange resins.

A Culligan HI-FLO 5 Water Softener Model 150* was installed and operated on the pad at well No. 3. The completely automatic water softener was converted to a semiautomatic anion exchanger by installing an industrial timer and anion exchange resin (Duolite A-101D). The system incorporated a 50.8-cm (20-in.) diameter bed that contained 123 L (4.36 ft^3) of anion exchange resin.

A pilot scale RO system producing 7.6 m^3/day (20,000 gpd) was operated on pretreated well No. 3 water. Ceilulose acetate spiral wound elements were used in this system.

Discussion of Results and Conclusions

Engineering Aspects

Ion Exchange

1. Design parameters for application of a conventional fixed single-bed ion exchange process with downflow regeneration for removal of nitrate from well waters were developed and tested using laboratory columns and a modified conventional automatic water softener converted to a 20-in. diameter anion exchange pilot column. The process is depicted in Figure 1 for a well water of moderate nitrate and sulfate levels. Pilot column tests were conducted using a Type I strong-base anion exchange resin (Duolite A-101D) at well 3. Because well No. 3 is high in nitrate (ca 20.3 mg/L NO_3-N) and sulfate (ca 320 mg/L), it is a useful research well.

2. The study shows that automatic ion exchange equipment, which is commonly used by the water softening industry, can be adapted for nitrate removal. The equipment can be installed at a well site for direct treatment of well water and operated on demand without storage.

3. The selected resin was effective for the nitrate removal for flow rates over 45 gpm/ft^2 of bed area (2.75 BV per minute). Forty five gpm/ft^2 was the upper limit of the test equipment used. These high flow rates bring the cost of capital equipment and resin quantities to low practical levels.

4. When sulfate is present in raw water, operating the ion exchange column in a partial regeneration mode is more economical than in the complete regeneration mode because the resin concentrates nitrate near the downstream end of the column from which it is easily removed. Salt requirements for McFarland wells ranged from 2.5 to 5 lb of sodium chloride/ft^3 of resin. In comparison, complete regeneration would require 18 to 20 lb/ft^3. The extended bed life and lower nitrate leakage does not justify the added salt costs for complete regeneration. Partial regeneration also produces a water less corrosive than the high chloride water produced by complete regeneration.

5. Capital equipment costs of an ion exchange system for treating a ½ mgd production well are estimated to be less than $100,000 installed (1981 costs). This estimate is based on moderate nitrate levels (less than 13.5 mg/L NO_3-N) in well water and sulfate levels less than 200 mg/L and on blending (50/50) treated water with raw water to produce a water less than 10 mg/L NO_3-N (see Figure 1). Equipment cost for a system to treat all water from a 1-mgd production well is estimated at less than $160,000.

The total water cost including amortized capital and operating costs are estimated to be 17.3 cents/1,000 gal (4.6 cents/m^3) of treated water. This is based on raw water nitrate-nitrogen levels of 13.5 mg/L, sulfate levels of 200 mg/L, and treated water nitrate-nitrogen levels of 6.8 mg/L with all sulfate removed. These costs do not include brine disposal costs, which are variable and community dependent. Brine disposal costs can be proportional to regeneration chemical costs if disposed to local landfills and could increase the above unit quantity costs by 30 to 50 percent.

6. Regenerant costs alone over a 20-year plant life can be more than double the first equipment costs of the plant. Because of the significance of regenerant costs, a method is presented to estimate the sodium chloride require-

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ments for regenerating the resin used in nitrate removal from waters of various composition. Because anion exchange resins are quite selective for sulfate ion, the presence of sulfate in raw water decreases the efficiency of the resin to absorb nitrate. In this study, however, the sodium chloride regenerant easily removed sulfate from the spent resin in nearly stoichiometric proportions whereas excess regenerant is required for nitrate removal. The overall effect of sulfate, however, is to increase the salt required to remove nitrate per unit quantity of water treated. This study also confirmed that large quantities of regenerant (20 lb/ft³ of resin) are required to remove most of the nitrate from the spent resin. Not all nitrate need be removed, however, to reduce nitrate-nitrogen levels in treated water to below 10 mg/L.

For McFarland wells, the salt requirements for lowering nitrate levels to between 6.8 and 10 mg/L NO_3-N range between an estimated 2.48 to 4.48 lb/ft³ of resin. The salt costs range between 2.31 cents/1,000 gal of blended (50/50) water for well No. 2 to 12.28 cents/1,000 gal of treated water for well No. 3. Well No. 3 represents a particularly difficult water to treat as nitrate-nitrogen levels are near 23 mg/L and sulfate levels are above 300 mg/L. Nitrate-nitrogen levels in well No. 2 are near 13.5 mg/L and sulfate levels are near 200 mg/L. Salt requirements for waters of other compositions are given (Table 1).

7. To achieve efficient nitrate removal, good brine and influent flow distribution are essential and may require modification in commercially available softening equipment. A method of declassification (thorough mixing) of the resin after downflow regeneration should also be incorporated in the regeneration cycle.

8. Wastewater produced during the regeneration cycle has an enriched composition of sodium sulfate, chloride, and nitrate. Continuous operation of well No. 2 would produce over 12,000 gal of wastewater/day (see Figure 1). Continuous operation of well No. 3 would produce an average of 39,000 gal of wastewater/day.

Reverse Osmosis

1. An RO system, operated on well No. 3 for over 1,000 hr, contained spiral wound cellulose acetate membranes and produced 15 gpm of treated water with 75 percent water recovery. Of the major groundwater anions, nitrate is

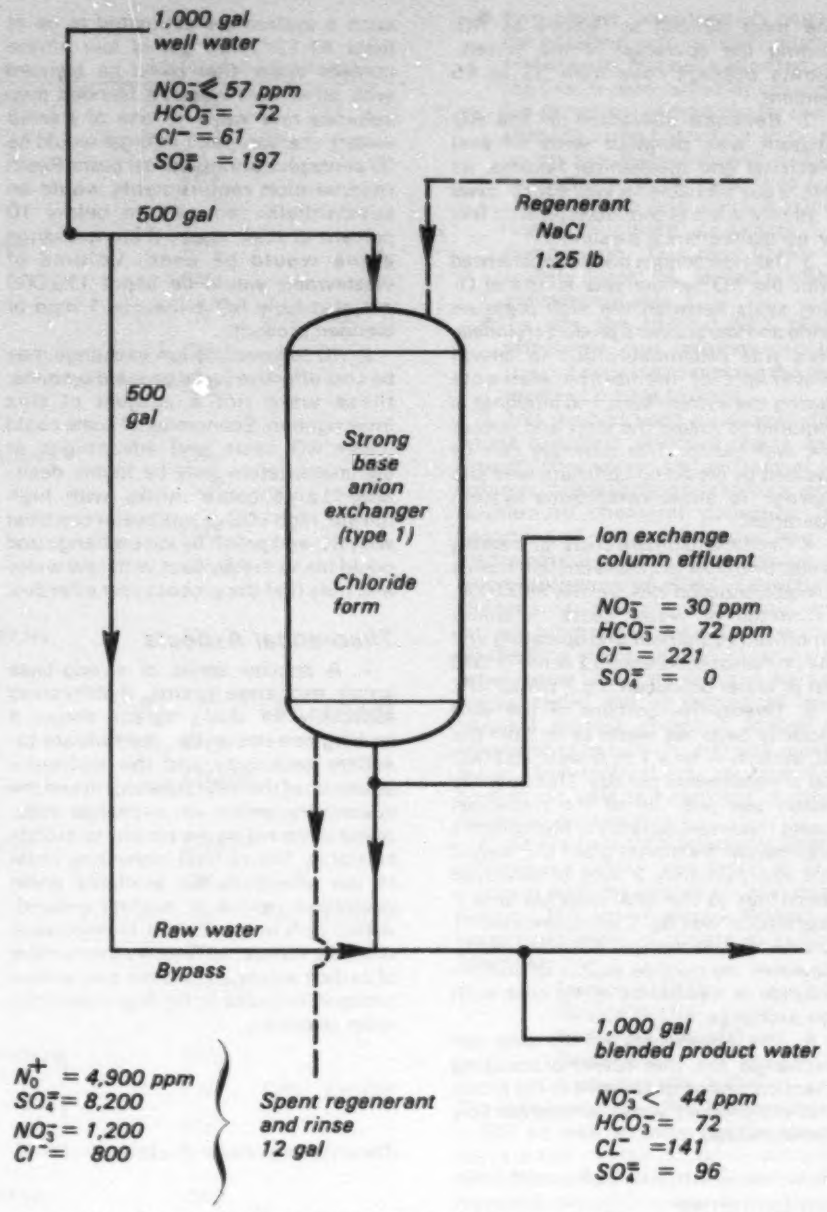


Figure 1. Conventional single-bed ion exchange process.

Table 1. Regeneration Requirements for Waters of Various Compositions

Water Composition	NO_3^- meq/L	1	1	1.5	1.5	1.5	1.5
	HCO_3^-	1	1	1	1	1	1
	Cl^-	1	1	1	1	1	1
Operating	$SO_4^=$	.5	3	3	2	1	.5
Parameter	Total Anion	3.5	6.0	6.5	5.5	4.5	4.0
NO_3^- in product water ppm		30	30	30	30	30	30
Bed volumes treated to breakthrough		423	229	207	247	307	347
Salt loading lb/ft³		2.15	3.73	4.13	3.67	3.36	3.22
Salt requirement lb/1,000 gal		0.68	2.18	2.67	1.98	1.46	1.24

the most difficult to remove by RO. During the operation of the system, nitrate passage rose from 33 to 65 percent.

2. Because operation of the RO system was plagued with several electrical and mechanical failures, its use is questionable for well site removal of nitrate in small communities with few or no maintenance personnel.

3. The most serious trouble experienced with the RO system was failure of O-ring seals between the high pressure brine and low pressure product channels. This was presumably due to lateral movement of membrane elements during the system start and stop that is required to follow the start and stop of the well pump. This difficulty can be avoided by providing sufficient well site storage to allow continuous system operation.

4. Capital equipment costs for treating water by RO for nitrate reduction from a 1-mgd production well are over $800,000. Estimates of water costs including amortized equipment and operating and maintenance costs are 99.2 cents/1,000 gal of water produced (26.2 cents/m^3).

5. Twenty-five percent of the well capacity becomes waste brine from the RO system — for a 1 mgd well, 250,000 gal of wastewater per day. This quantity would use one-half of the municipal waste treatment capacity of McFarland's wastewater treatment plant and would add approximately 2 tons of dissolved solids/day to the local disposal area if operated at well No. 2 (compared with 1 ton for ion exchange — same basis). However, no outside source of sodium chloride is needed as is the case with ion exchange.

6. The advantages of RO over ion exchange are that fewer processing chemicals need be brought to the locale and the product water is considerably demineralized.

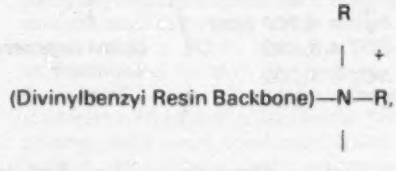
Reverse Osmosis Followed by Ion Exchange

1. For small communities, there appears to be few advantages to using RO followed by ion exchange polishing to produce water of low nitrate content (less than 1 mg/L NO_3-N). Because RO brine was ineffective for regenerating the nitrate-loaded resin, some salt was still required. The added complexity and cost of operating an RO system in conjunction with ion exchange at the well site appears to outweigh any advantages of producing a less mineralized water. Water costs by operation of such a system are estimated to be at least $1.12/1,000 gal of low nitrate content water that could be blended with other well water. If blended (two volumes raw water to one of treated water), the cost per 1,000 gal would be 37 cents plus brine disposal costs. Resin regeneration requirements would be substantially reduced, to below 10 percent of their value, if ion exchange alone would be used. Volume of wastewater would be about 115,000 gal of mainly RO brine per 1 mgd of blended product.

2. RO followed by ion exchange may be cost effective for large scale systems; these were not a subject of this investigation. Economies of scale could lower RO costs and advantages of demineralization may be highly desirable. Large communities with high nitrate, high TDS groundwater can treat with RO and polish by ion exchange and could blend the product with raw water and may find the process cost effective.

Theoretical Aspects

1. A special series of strong-base anion exchange resins, synthesized especially for this program, shows a striking correlation between nitrate-to-sulfate selectivity and the molecular structure of the alkyl substituents on the quaternary amine ion exchange sites. Some of the resins are nitrate-to-sulfate selective. The normal increasing order of ion selectivity for available anion exchange resins at normal groundwater concentrations is bicarbonate, chloride, nitrate, sulfate. As the number of carbon atoms around the ammonium nitrogen increase in the R groups of the resin structure,



the increasing order of ion selectivity is changed to bicarbonate, chloride, sulfate, nitrate. Where R is methyl, K_S^N (a measure of nitrate-to-sulfate selectivity) is approximately 100; whereas if R is ethyl, K_S^N is approximately 1,000. Thus, in column tests with the triethyl resin on water having a nitrate plus sulfate concentration of greater than 8 meq/L, nitrate is the last ion to breakthrough. Other resins with a total of four and five carbon atoms show intermediate K_S^N values. See Tables 2 and 3 and Figure 2. The effect of introducing OH groups into the alkyl substituents is to decrease the K_S^N value. For example, if the R groups are ethoxy, the K_S^N value is approximately 10.

These structural effects on K_S^N value are ascribed to steric strains set up in the resin by the special (or steric) requirements of alkyl R groups with nitrate having capability of decreasing the steric strain whereas sulfate can increase strain. Little effect on the K_C^N values are noted. All resins are easily regenerated with chloride brines. This observed effect of molecular structure gives rise to a concept of structurally induced electroselectivity reversal.

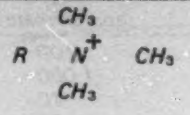
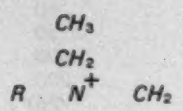
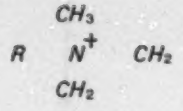
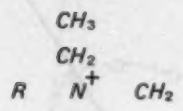
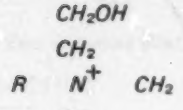
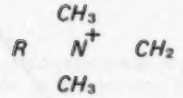
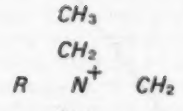
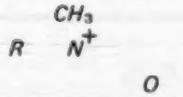
2. The net effect of using the triethyl amine resin as compared with the commercially available trimethyl resin, is to increase the bed life BV (N) from 170 to 275, an increase of 62 percent, when treating a water containing 1.5 meq/L nitrate and 6.5 meq/L sulfate (see Figure 3). The immediate effect is to reduce wastewater for processing by 38 percent. A second desirable effect of using the triethyl resin is to reduce by 25 to 50 percent, the amount of regenerant required to remove an equivalent amount of nitrate depending on the mode of operation and level of regeneration selected. This represents a projected cost savings of $84,000 to $168,000 in salt over the 20-year plant life plus at least equivalent amounts for brine disposal costs. Special column operation must be used since the nitrate breakthrough can be compounded and a choice is available to operate to the first or second nitrate breakthrough. A third advantage in using NSS resins is to preserve more of the raw water quality by allowing sulfate to pass through the column.

3. The structural effects noted above were found characteristic of a series of eight special resins that show a trend toward increased K_S^N (and greater process efficiency) without any observable limit. Consequently, it is believed a continuing study of structural changes can produce an optimum resin that will give an even greater cost saving than that noted above.

4. The nitrate-to-sulfate selective (NSS) resins have characteristics that require special consideration in process design.

- Anion exchange capacity of NSS resins is approximately 15 percent lower than their Type 1 counterpart.

Table 2. *Structures of Special Resins*

No.	Designation	Amine	Molecular Structure*
1	R-TM	Trimethyl	
2	R-TE	Triethyl	
3	R-MDE	Methyldiethoxy	
4	R-EDEOH	Ethyldiethoxy	
5	R-TEOH	Triethoxy	
6	R-DMEOH (same as A-104)	Dimethylethoxy	
7	R-DEEOH	Diethylethoxy	
8	R-N-MM	N-methyl-morpholine	

*R denotes resin backbone structure.

- Two nitrate breakthrough points are obtained with partially regenerated resin. Nitrate leakage before the first is determined by chloride ion-nitrate ion competition for resin sites. The first breakthrough point occurs simultaneously with sulfate breakthrough. Nitrate leakage after sulfate breakthrough is determined by nitrate ion-sulfate ion competition. The first break is usually sharp; the second is often indistinguishable.
- To use the triethyl NSS resin effectively, two columns can be run out of phase to average the two levels of nitrate leakage.

5. The method used to discover the nitrate-to-sulfate selective resins was through observation and analysis of (a) column breakthrough profiles and relation to chemical structure; (b) departure of column behavior from a mathematical model; (c) the shape of binary isotherms; (d) effect of structural changes on primary, secondary, and tertiary ammonium weak-base resins; (e) swelling effects of ions on resins; (f) experiments on nitrate-selective sulfate-loaded resin; and (g) inferences from physical organic chemical studies of effects of structure on chemical equilibrium. This method may be applied to studies on selective removal of other inorganic contaminants.

6. Nitrate-to-sulfate selectivity among strong-base resins was found to also increase with the degree of resin cross linking. The list of resins studied in increasing order of nitrate-to-sulfate selectivity are:

Duolite A-101D
Duolite A-104
Amberlite IRA-910
Dowex SAR
Amberlite IRA-900

The literature shows IRA-410 and Ionac A-550 as well as some tertiary amine weak-base resins to have nitrate-selective tendencies. However, commercially available resins do not show enough nitrate selectivity to be of significant value. In this study they are not NSS resins. Lower anion exchange capacity is a disadvantage of the higher cross linked resins and also makes the ion exchanger appear to be nitrate-to-sulfate selective through the electroselectivity effect. (Activated carbon is a notable case.) Also, where nitrate and sulfate are equal in selectivity, the spent column will have nitrate evenly distributed in the column. This is a disadvantage in downflow regeneration

Table 3. Properties of Special Resins[1]

No. and Designation	Moisture[2] Content (%)	Vol. Capacity[2] (eq/L)	K_S^N (approximate)	NSS
1 R-TM	51.0	1.41	100	-0.14
2 R-TE	47.9	1.19	1,000	+0.92
3 R-MDEOH	41.1	1.41	10	-1.15
4 R-EDEOH	38.9	1.30	50	-0.41
5 R-TEOH	33.1	1.23	10	-1.09
6 R-DMEOH[3]	45.7	1.42	50	-0.45
7 R-DEEOH	43.5	1.29	100	-0.11
8 R-N-MM	44.6	1.35	200	+0.17
(Duolite A-101D)	(48 to 55)	(1.3)	(25)	-0.71

[1]All resins synthesized from the resin intermediate used in commercial manufacture of Duolite A-104.
[2]Data supplied by Diamond Shamrock.
[3]Same as Duolite A-104.

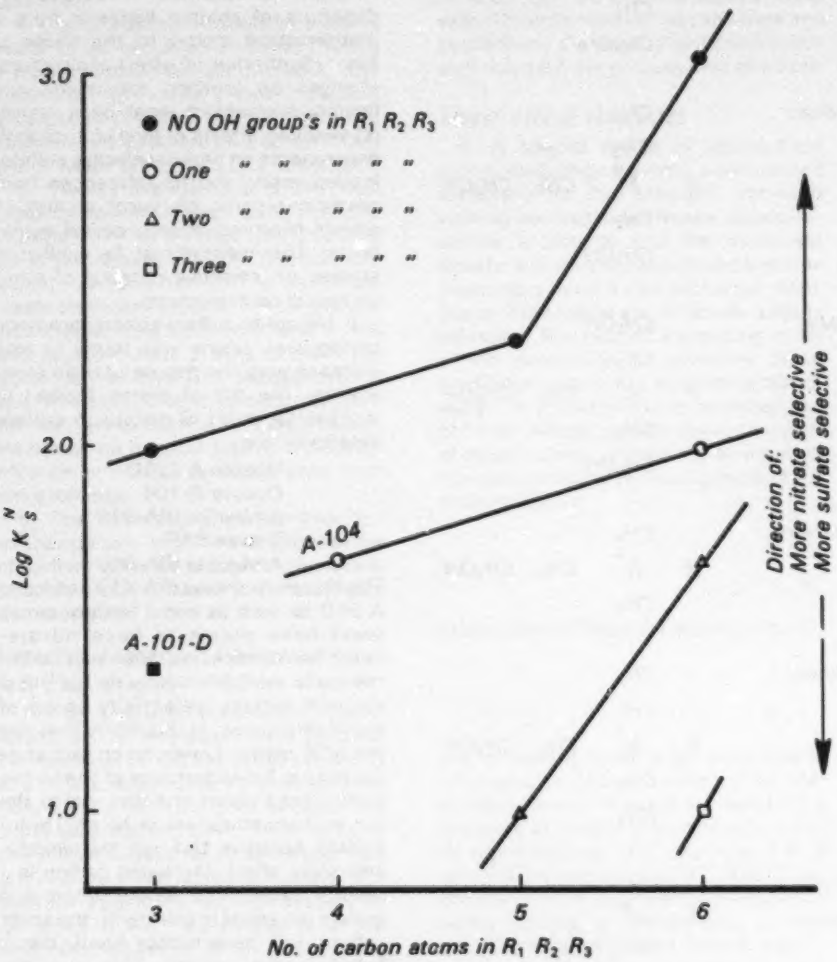


Figure 2. Effect of structure on nitrate to sulfate selectivity.

since nitrate must be moved through the entire column. Consequently, A-101D resin was chosen for pilot studies because nitrate concentrates near the exit end of the column from which it is more easily removed during regeneration. It is also pointed out in the study that threshold K_S^N values must be reached before a resin can be a nitrate-to-sulfate selective resin and before process efficiency can be improved.

7. Use of chemical regenerants other than sodium chloride was briefly explored. It was demonstrated that nitrate can be selectively removed using sulfate-loaded resins. It is suggested that dilute calcium sulfate be tested as a regenerant. Larger volumes of regenerant using a low TDS water are required. Such a supply is available in McFarland as irrigation water. Waste brine would contain calcium nitrate and sulfate both of which are disposable to agricultural lands. Ammonium chloride is also suggested as regenerant that would give ammonium nitrate and sulfate as a disposable brine.

8. From these studies and a review of previous studies on synthesis of resins with higher nitrate-to-chloride selectivity, it does not appear regenerant requirements can be reduced if nitrate-to-chloride selectivities are increased. Available anion exchange resins are already nitrate-to-chloride selective. Making them more selective for nitrate will only add to further regeneration inefficiencies. This, however, does not appear to be the case with the NSS resins since the nitrate-to-chloride selectivities did not change substantially whereas nitrate-to-sulfate selectivity did change.

Recommendations

1. An ion exchange demonstration plant of ½- to 1-mgd capacity should be installed and operated to obtain actual operational experience regarding reliability, health, safety, and costs. Commercially available resins should be used because NSS resins require further testing.

2. As pointed out above, the cost of regenerant and brine disposal over the plant lifetime can be several times the cost of the plant. Efforts should be made to reduce regenerant requirements to the lowest level practicable. This can be done by recycling portions of brine and brine rinse as well as backwash waters in demonstration plant operation and continuing studies on nitrate-to-sulfate selective resins.

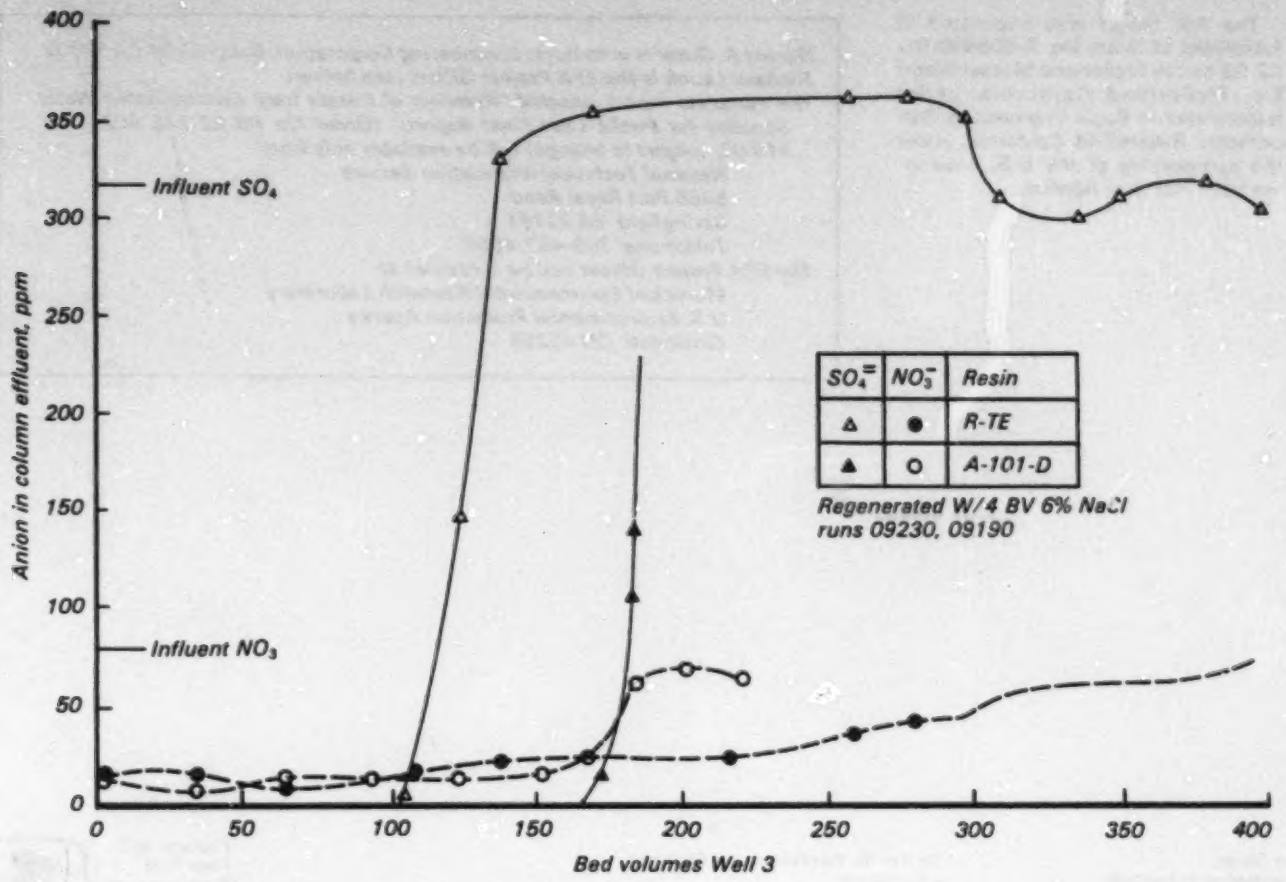


Figure 3. Ion exchange column experiment 09230 and 09190.

3. Studies should be conducted on use of regenerants other than sodium chloride for the single-bed process to produce waste brines more amenable to disposal on agricultural land.

4. Studies on NSS resins should continue since further increases in nitrate-to-sulfate selectivity can be expected. These resins must also be characterized as to fouling tendency, chemical degradation, and acceptance in water treatment.

5. Brine disposal is the single most important factor and major expense that deters widespread use of the ion exchange process. All future efforts to improve the process should focus on this impediment to its application.

6. Ion exchange is recommended over RO for nitrate removal at remote well sites in small communities because of cost and operational problems associated with RO. This study showed that total costs for treatment of well No. 2 water were approximately 18 cents/1,000 gal for ion exchange versus $1/1,000 gal for RO. Brine disposal costs were not included in either estimate.

Summary

The ion exchange process is generally more suitable as a well site treatment for nitrate removal than RO or a combination of the two. Ion exchange requires lower first cost and annual operating costs, has greater reliability, uses less energy, requires no additional well site storage, has higher water recovery, produces a more concentrated waste brine, and requires fewer automatic and electrical controls. It can be operated on demand as required by distribution system needs. Such on-off operation is severely detrimental to an RO system, which operates best on a continuous basis and, hence, requires additional storage and repressurization. Brine disposal is a cost common to both processes.

Ion exchange resins with altered chemical structures were formulated for selective removal of nitrate from common groundwaters containing sulfate ions. Projected use of nitrate-to-sulfate selective (NSS) resins in ion exchange plants has potential to reduce operating costs by increasing the efficiency of the process through reduced wastewater, reduced brine requirements, and lower waste brine disposal costs. These operating cost savings are estimated to exceed the equipment costs of the plant over a 20-year period. The NSS resins, which require further testing before practical applications can be made, are presently not commercially available. Small quantities were made for this program by a resin manufacturer using existing processes and available intermediates. The NSS resins are examples of structurally induced electroselectivity reversal, a concept that may find applications in removal of other contaminants.

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***Richard Lauch** is the EPA Project Officer (see below).*
The complete report, entitled "Removal of Nitrate from Contaminated Water Supplies for Public Use: Final Report," (Order No. PB 82-222 902; Cost: $18.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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The EPA Project Officer can be contacted at:
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
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Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300

RETURN POSTAGE GUARANTEED

Third-Class
Bulk Rate